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Short communication

Effect of cathode microporous layer composition on proton exchange membrane fuel cell performance under different air inlet relative humidity

Hong-Hua Chen, Min-Hsing Chang*

Department of Mechanical Engineering, Tatung University, Taipei 104, Taiwan

HIGHLIGHTS

► Performance at different air relative humidity depends on cathode MPL composition.
► The optimal PTFE content was explored at different air relative humidity.
► The optimal loading of acetylene black is independent of the air relative humidity.
► Composite carbon black could enhance cell performance at low air relative humidity.

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ABSTRACT

The effects of cathode microporous layer (MPL) composition including carbon black and polytetrafluoroethylene (PTFE) loadings on the performance of a proton exchange membrane fuel cell (PEMFC) are evaluated under different relative humidity (RH) at air inlet. Both acetylene black and composite carbon black which is made of acetylene black and black pearls 2000 (BP) are used in the experiments. The results show that the optimal cell performance at different air RH depends on the cathode MPL composition. When acetylene black is used, the optimal composition at higher RH is found to be 1.5 mg cm^{-2} carbon loading and 20 wt% PTFE content, while an increase in PTFE content could improve the cell performance at lower RH states. The cell performance also could be enhanced significantly at lower RH when composite carbon black is employed, while it fails to increase the cell performance at higher RH. The composite carbon black with 30 wt% BP is found to give the optimal cell performance at low RH conditions. The results benefit the understanding for the role of cathode MPL in running PEM fuel cells under insufficient air humidification.

1. Introduction

The air humidity plays an important role in the factors affecting the performance of a proton exchange membrane fuel cell (PEMFC). In order to simplify the fuel cell structure and eliminate the complicated humidification system, one of the developing trends in PEMFC design is trying to make the Membrane-Electrode-Assembly (MEA) of a PEM fuel cell can still operate properly under low air relative humidity (RH) condition without any humidification device. To achieve this goal, it is important to evaluate the role of microporous layer (MPL) for running PEMFC at low RH conditions especially in the cathode site.

The MPL coated on the surface of gas diffusion layer (GDL) is a critical factor dominating the MEA performance. Numerous studies have been devoted to the investigation of the MPL and explored its importance in the factors affecting the fuel cell performance. The MPL is generally composed of carbon black and hydrophobic agent like polytetrafluoroethylene (PTFE) or fluorinated ethylene propylene (FEP) which is a thin layer next to the catalyst layer. The employment of MPL has been found that it may lower the liquid water saturation in the cathode side and thus improve the water transport performance. On the other hand, it also may reduce the gas permeability since it is made of fine carbon black and thus may result in higher gas transport resistance. Accordingly, it is an important issue to understand the effect of MPL composition on the cell performance in order to operate a PEMFC under low RH condition in the air stream. Recently, several investigations focusing on the degree of humidification in air stream and its influence on cell performance have been proposed [1–5].

* Corresponding author. Tel.: +886 2 21822928x6172; fax: +886 2 25997142.
E-mail address: mhchang@ttu.edu.tw (M.-H. Chang).

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Kannan et al. [1] designed a functionally graded nano-porous GDL and evaluated its performance in a single PEMFC under various operating temperature and RH. They observed that the functionally graded nano-porous GDL showed an excellent performance at 85 °C with air at 50% RH. Kitahara et al. [2] studied the influence of MPL design parameters on the performance of a PEMFC. The commercial carbon paper (SGL SIGRACET® 24BA) was used as the GDL substrate and the RH of air supplied at the cathode was set at either 100% or 0%. They found that under low humidification conditions, decreasing both the pore diameter and the content of PTFE in the MPL is effective to prevent drying-up of the MEA and enhance the cell performance. Effects of cathode inlet RH on the durability of a PEMFC during startup–shutdown cycling have been explored in details by Kim et al. [3,4]. Kundu et al. [5] focused on the effects of RH on the chemical degradation of the membrane during open circuit voltage testing. They proposed a chemical degradation model of the ionomer membrane to simulate their results. In these related studies, only the work of Kitahara et al. [2] has considered the effect of MPL composition on the cell performance at extremely different RH in air flow. However, the type of carbon black used in their experiments is unclear. The related investigations are still quite limited, which motivates the present work.

In this study, the influences of cathode MPL composition including carbon black and PTFE on PEMFC performance are evaluated under different RH in air stream. Various carbon blacks are employed in the experiments and the results are discussed to clarify the importance of MPL composition in the factors affecting the cell performance at different air RH conditions, and suggest the optimization of cathode MPL composition.

2. Experimental

2.1. Preparation of gas diffusion media and MEA

To make the gas diffusion media, SGL® 10BA carbon paper with 5 wt% PTFE content was used as the substrate for cathode GDL. The paper was washed with acetone before MPL coating to remove possible surface contaminants. For MPL coating, a carbon slurry was first prepared from a mixture of carbon black and ethylene glycol with a pre-assigned weight percentage of PTFE. The mixture was sonicated in an ultrasonic cleaner and then agitated by a dispersing instrument for 1 h in each process to ensure sufficient mixing of the carbon black and PTFE. Next, the slurry was sprayed uniformly on the surface of the carbon paper to form the MPL, followed by drying in a convection oven at 90 °C. This spraying and drying process was repeated several times until the carbon loading reaches the assigned value. Finally, the carbon paper was drying further at 240 °C for 30 min and then sintered in a high-temperature oven at 350 °C for 40 min to complete the MPL coating. The types of carbon black used in the experiments include acetylene black and composite carbon black made of acetylene black and BP 2000. The detailed specifications of these carbon blacks could be found in the works [6]. All the experiments used SGL® 10BC carbon paper as the gas diffusion media in the anode side. The MEA was assembled by a catalyst-coated proton exchange membrane (CCM, Nan-Ya®, bMEA5) with both anodic and cathodic gas diffusion media on opposite sides of the CCM. The active reaction area of the MEA is 5 cm × 5 cm.

2.2. Operating condition and performance tests

A single cell fixture, comprising the MEA, graphite flow field plates, current collectors, and end plates was connected to a Hephas® P-300 fuel cell test station to measure the cell performance and obtain the polarization curves. The graphite flow field plates were machined by a parallel serpentine flow channel design. Pure hydrogen and air were used as the fuel and the oxidant, respectively. Both reactant gases were humidified by bubbling the gases through distilled water tanks held at an assigned temperature. Humidified hydrogen gas was held at a constant temperature 70 °C and humidified air was controlled at various temperatures (30–70 °C) at the exit of water tank. Both hydrogen and air streams flow through an electrical heating pipeline to enter the fuel cell. All the temperatures were monitored by burying thermocouples at the exits of water tanks and the gas inlets of fuel cell. The heating power of pipeline is adjustable to make sure the air flow enter the fuel cell at 70 °C. In order to obtain steady gas temperature at the gas inlets of fuel cell, humidified hydrogen and air were respectively delivered at constant flow rates 600 and 2000 sccm in all the tests. The RH of air at the exit of water tank was calibrated at different temperature to ensure the air stream was fully humidified as it left the tank. Accordingly, we may determine the RH at the air inlet of the fuel cell based on the temperature difference. By adjusting the air humidification temperature between 30 and 70 °C, the RH of air at inlet may vary between 13.6 and 100%. The fuel cell temperature is also held at constant temperature 70 °C by electrical pipe heater. The method of electrochemical impedance spectroscopy (EIS) was used to identify the contributions of cell resistance. A frequency response analyzer (FRA) module added to an Autolab PGSTAT 302Ntentiostat was employed to perform the EIS measurements. The impedance spectra were recorded by sweeping frequencies over the range of 10 μHz to 1 MHz with the amplitude of the AC current held at 5% of that of the DC current. The obtained spectra were further analyzed by an equivalent circuit to explore the variations of ohmic resistance, charge transfer resistance, and gas transfer resistance.

3. Results and discussion

We first consider the effects of PTFE content and carbon loading in cathode MPL, and then examine the influence of composite carbon black. The optimal MPL composition is discussed by evaluating the variations in the peak power density and impedance spectra under different RH in air stream.

The polarization curves for the typical case of 5 wt% PTFE content in cathode MPL at different air RH are shown in Fig. 1 with acetylene black as the carbon black. It is obvious that the effect of air RH is quite significant and the cell performance depends heavily on the degree of humidification in the air stream. The cell performance presents the best state at fully humidification condition and degrades gradually with decreasing air RH. Similar results also can be observed at the other cases with higher PTFE contents. The results are summarized as displayed in Fig. 2 by illustrating the variations of the peak power density with the air RH. The carbon loadings are fixed at 1.5 mg cm^{-2} in all the tests. One can see that at fully humidified condition (100% RH), the peak power density first increases with increasing PTFE content, reaches maximum at 20 wt %, and then begins to descend. This result reveals that the PTFE content is an important factor dominating the cell performance. Similar variations also can be observed at moderate air RH conditions. However, when the air RH is less than 40%, the case of 30% PTFE exhibits better cell performance than that of 20% and gives the highest peak power density in the low RH region. But both results are still quite close. Once the PTFE content increases further over 30%, a significant reduction in cell performance occurs in each case of assigned air RH. These results indicate the optimal PTFE content is approximately 20% at high air RH conditions, while a higher PTFE content about 30% would be beneficial to run the cell under low air RH conditions. The function of MPL is known to enhance the water transport performance within the gas diffusion media especially in

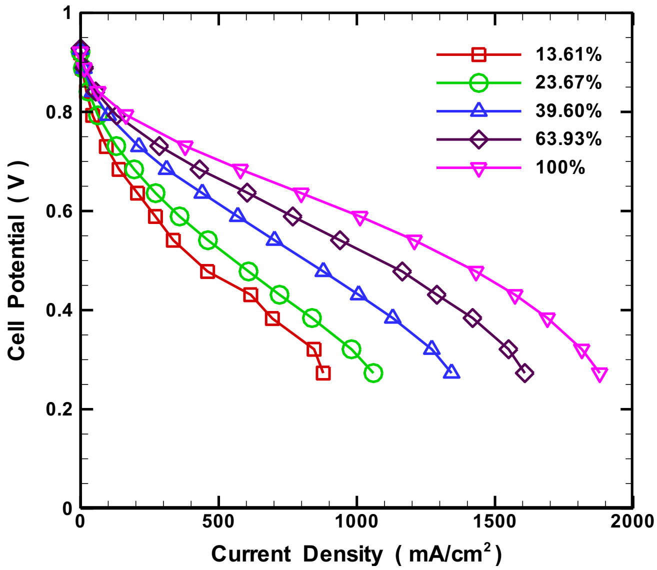

Fig. 1. Polarization curves at different air RH. The PTFE content is 5 wt.% and carbon loading is 1.5 mg cm^{-2} in the cathode MPL. Cell temperature 70 °C and constant flow rates of 600 and 2000 sccm for hydrogen and air, respectively.

the cathode side. Obviously, the influence of PTFE content in the MPL is prominent at any air RH state. An appropriate PTFE content in the MPL is beneficial to reduce the liquid water saturation within gas diffusion media, avoid the occurrence of flooding phenomenon, and thus enhance the transport performance of gas reactants. This effect is still significant even though at low air RH conditions.

To further explore the effects of PTFE content, electrochemical impedance spectroscopy (EIS) was used to diagnose the variations of cell performance under different air RH conditions. For example, the impedance spectra at a current density of 1.0 A cm^{-2} as a function of air RH are shown in Fig. 3 for the case of 20% PTFE content. Two distinct arcs are observed in each curve, which are typical spectra for a hydrogen/air PEM fuel cell. The horizontal real axis intercept of the impedance spectrum at the end of the left arc represents the ohmic resistance of the fuel cell. As illustrated in Fig. 3, the ohmic resistance increases and shifts significantly to the

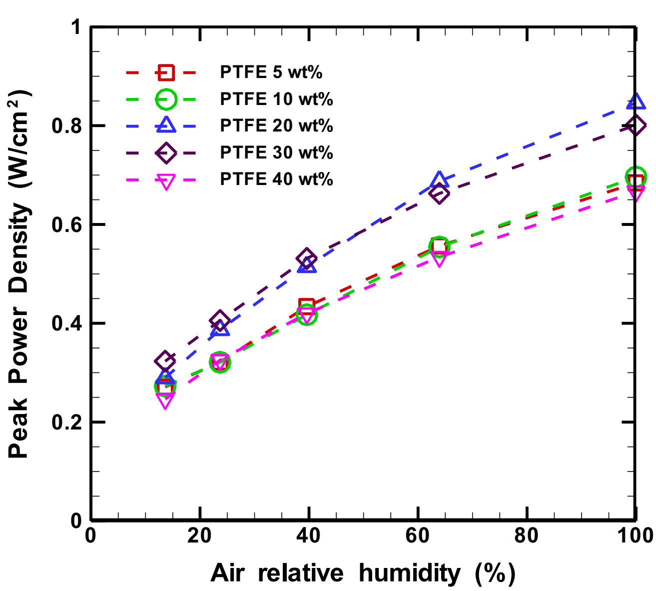

Fig. 2. Variations of peak power density with air RH at different PTFE contents in the cathode MPL. Cell temperature 70 °C and constant flow rates of 600 and 2000 sccm for hydrogen and air, respectively.

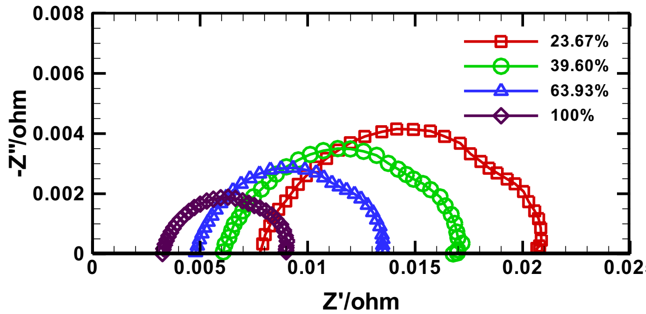

Fig. 3. Impedance spectra at different air RH measured at current density 1 A cm^{-2} for the case of 20% PTFE content.

right with decreasing air RH. Since the ohmic resistance is mainly contributed by the membrane resistance, it is obvious that the decrease of air RH reduces the water content in the membrane and thus increases the transport resistance of proton through the membrane causing the rise of ohmic resistance. The high-frequency arc on the left represents the effective charge transfer resistance for the oxygen reduction reaction in the catalyst layer, and the low-frequency arc on the right is attributed mainly to the transport resistance of air within the gas diffusion media. Obviously, both the left and right arcs grow gradually with decreasing air RH. A generally proposed equivalent circuit [7] was used to simulate the impedance data for a fuel cell operating at high current density condition. The results showed the cell performance is primarily dominated by the ohmic resistance and charge transfer resistance, while the gas transfer resistance is relatively negligible under the test condition. It is found that both cases of PTFE content 20% and 30% give the minimum ohmic and charge transfer resistances at higher and lower air RH conditions, respectively. But the differences between both results are quite small in each case of assigned air RH. The EIS results reveal that an appropriate PTFE content in the cathode MPL could improve the maintenance of water content in the membrane and the electrode kinetics performance, and thus reduce the activation overvoltage even at low or moderate air RH conditions.

The carbon loading in cathode MPL is the other important factor which should be evaluated. The results are shown in Fig. 4 for the variations of peak power density with air RH at different carbon loadings. The PTFE content is fixed at 20 wt% in all the tests. It is obvious that the cell performance is sensitive to the variation of carbon loading in each case of assigned air RH. For a given air RH, the peak power density generally rises with increasing carbon loading, reaches a maximum at 1.5 mg cm^{-2}, and then decreases gradually. The optimal carbon loading is always the same and independent of the air RH. The corresponding EIS tests were also performed at current density of 1.0 A cm^{-2} as a function of air RH. The results show that both ohmic and charge transfer resistances always decreases gradually with increasing air RH in each case of carbon loading. Particularly, the case of 1.5 mg cm^{-2} always gives the lowest resistances under the same air RH condition. That is, under low or moderate air RH states, an appropriate amount of carbon loading is still quite important to improve the dehydration phenomenon of membrane and thus reduce the ohmic resistance. It is also helpful for enhancing the catalyst utilization rate, increasing the number of possible reaction sites, and accordingly lowering the charge transfer resistance.

The effect of composite carbon black which is made of acetylene black and Black Pearls 2000 (BP) is also considered in the present work. It has been found in the work [6] that the employment of such a composite carbon black may construct an effective bi-functional MPL and obtain an optimal cell performance with

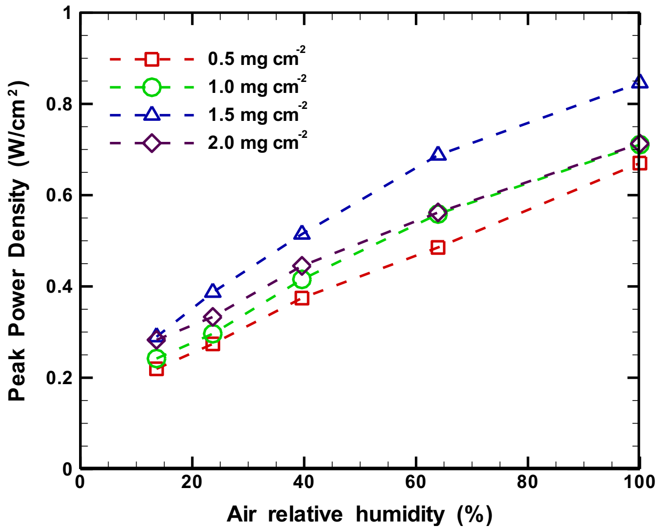

Fig. 4. Variations of peak power density with air RH at different acetylene black loadings in the cathode MPL. Cell temperature 70 °C and constant flow rates of 600 and 2000 sccm for hydrogen and air, respectively.

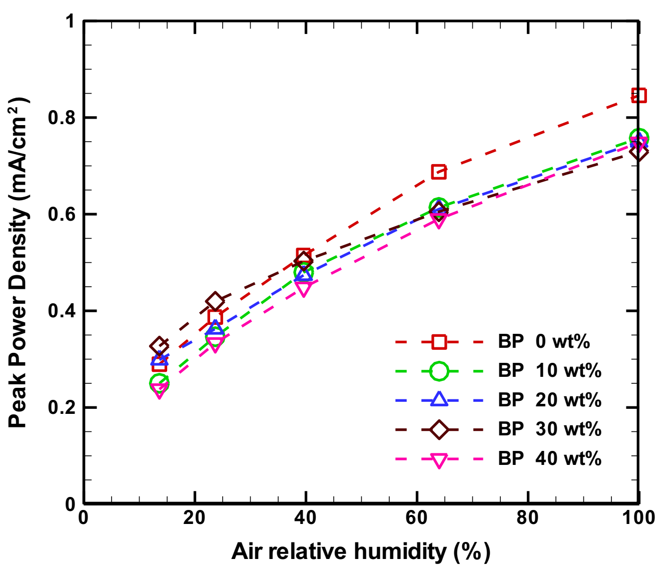

Fig. 5. Variations of peak power density with air RH at different BP content in the composite black. Cell temperature 70 °C and constant flow rates of 600 and 2000 sccm for hydrogen and air, respectively.

appropriate mixing ratio of both carbon blacks. The employment of composite carbon black may change the internal pore structure in the MPL and thus provide better transportation performance for both reactant gases and liquid water. Accordingly, the overall transport characteristic as well as the cell performance could be improved. The polarization curves at different air RH for several cases of composite carbon black with various concentration of BP were measured. The results are summarized by showing the variation of peak power density with air RH as demonstrated in Fig. 5. The carbon loading and PTFE content in each case are fixed at 1.5 mg cm^{-2} and 20 wt%, respectively. When the air stream is fully humidified or in moderate value of RH, the present results show that the utilization of composite carbon black does not provide any significant improvement in cell performance. Conversely, the peak power density is lowered after the usage of composite black in the MPL. The possible reason for this discrepancy between the present study and the work [6] is due to the differences in the MPL structure and composition. In the study of Wang et al. [6], the MPL was coated on both sides of GDL symmetrically with total carbon loading 1.0 mg cm^{-2} and PTFE content in MPL is 30 wt.%, which are quite different from those of present work with the MPL coated on the side facing to the catalyst layer only. These differences may cause the variation in pore structure within the gas diffusion media and affect the characteristics of mass transportation. However, under low air RH conditions (<40%), the composite carbon black indeed exhibits better cell performance with appropriate BP content. It is found that the case of 30 wt% BP content gives the highest peak power density at low air RH states. The corresponding EIS analysis also shows that this case presents the lowest ohmic and charge transfer resistances when the humidification of air stream is seriously insufficient, which indicates the employment of composite carbon black could promote the PEM fuel cell performance under low air RH circumstances.

4. Conclusions

The influence of cathode MPL composition on PEM fuel cell performance under different air RH is reported in this work. Various types of carbon black, including acetylene black and composite carbon black, are considered and the effect of PTFE content is also examined. The results show that the composition of cathode MPL indeed plays an important role in the factors affecting the fuel cell performance under low air RH condition. The optimal composition seems to be dependent on the air RH. In the case of acetylene black, the optimal composition is found to be 1.5 mg cm^{-2} carbon loading with 20 wt% PTFE content at high air RH conditions. While an increase in PTFE content exhibits better cell performance at low air RH conditions. The employment of composite carbon black shows that it could enhance the cell performance when the humidification is insufficient in air stream. But at fully humidification condition, the case of pure acetylene black still gives the better cell performance. Further experiments using other types of carbon black and hydrophobic agent in cathode MPL would be helpful for the investigation to run a PEM fuel cell without any humidification device in air stream.

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